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## Dithizone as an Analytical Reagent

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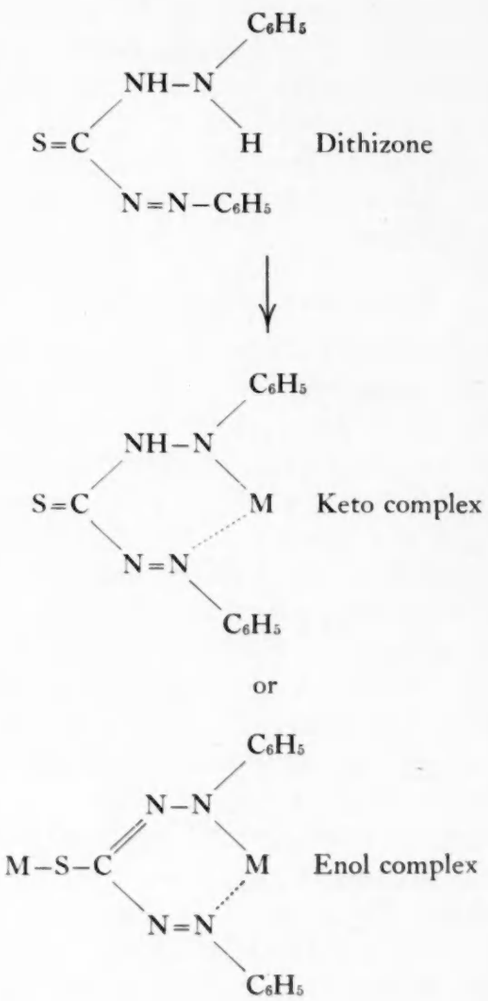
The analytical chemist has long recognized the usefulness of extraction methods which, in general, permit the simultaneous separation and concentration of a substance to be determined. In many cases, traces of the desired element may be separated from massive amounts of foreign material by relatively simple extraction procedures. When Emil Fischer (1) prepared diphenylthiocarbazone, also commonly called dithizone, he provided the analytical chemist with a tool of extraordinary possibilities. Some metal dithizonates are intensely colored and can readily be concentrated in a small volume of chloroform or carbon tetrachloride. The resulting solutions serve as the basis of a colorimetric technique, having a sensitivity which approaches, and sometimes actually exceeds, that of the spectrographic method.

Although Emil Fischer noted that dithizone produced intense colors with some of the heavy metals, no analytical applications were attempted until 1925, when Helmut Fischer (2) and his coworkers published the first in a long series of papers which clearly demonstrated the usefulness of dithizone as an analytical tool. Since then an extensive literature has appeared concerning its applications and reactions (3).

It is now well established that metal dithizonates may exist in either a so-called enol or keto form. These terms are not strictly correct but serve to differentiate between the two forms of the metal complex. The following formulae will serve to illustrate the reactions involved in which a hydrogen ion is replaced by a monovalent metal ion (M) and an inner complex compound is formed.

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The keto-metal complexes are soluble in organic solvents and are much more important from the analytical point of view than the enol complexes which are, at best, only sparingly soluble. Dithizone itself is soluble in many organic solvents, of which only chloroform and carbon tetrachloride have been used extensively, and in these it forms deep green solutions. It is only slightly soluble in dilute acids, but very soluble in alkalies and ammonia, to which it imparts a deep yellow color.

The usual method is to bring together a solution of dithizone in chloroform or carbon tetrachloride and an aqueous solution of the metal. The close contact which occurs when the two phases are shaken together in a separatory funnel provides an opportunity for the metal and the dithizone to react. Under favorable conditions, the metal dithizonate is formed quantitatively, and, because of its favorable partition coefficient, is found almost entirely in the organic layer when equilibrium has been established. The excess reagent also partitions between the two phases. Whether a larger or smaller fraction remains in the aqueous phase depends mainly on the pH maintained.

## Analytical Methods

The analytical techniques utilizing this reagent vary, but all may logically be placed in one of three general categories (4) (5). In the so-called "mono-color" technique, the metal dithizonate is formed and extracted into the organic phase together with all or part of the excess dithizone, which is then removed by shaking with an alkaline solution. The color is due to the metal dithizonate alone, and is measured in a photometer or compared with a suitable series of standards.

In the "mixed color" method, the excess dithizone is allowed to remain in the organic layer with the metal dithizonate. The result, when analyzing for lead, for example, is a solution having a hue intermediate between the green of pure dithizone and the red of lead dithizonate, depending upon the relative amounts of the two components present. The light absorption due to the metal dithizonate may be read with a photometer using a suitable filter to eliminate interference resulting from the excess dithizone. In this method, it is equally feasible to measure the absorption of the unreacted dithizone by the selection of the proper filter. This quantity also serves as a measure of the amount of metal present when subtracted from the absorption of the dithizone originally used. The success of this approach depends upon the fact that few of the metal dithizonates absorb in the same region of the spectrum as dithizone itself. Platinum and palladium, which form greenish dithizonates, are exceptions. Visual comparison of the mixed color with a series of standards can also be carried out satisfactorily. Fischer and Weyl (6) have given the spectral absorption curves of many of the dithizonates in carbon tetrachloride.

In the "titrimetric" or "volumetric" method, small increments of dithizone solution are added successively to the aqueous solution containing the metal to be determined. Shaking the solution and withdrawing the organic phase after each addition permits the selection of that increment in which the green color of dithizone remains unchanged because all of the metal has reacted. The end point can be made very sharp. The dithizone is standardized by the same procedure against known quantities of the metal.

The relative merits of each of these techniques depend upon the peculiar analytical situation involved. Generally speaking, the "mixed color" method is to be preferred, since it involves fewer operations and hazards than either of the other two. The removal of the excess dithizone in the "mono-color" method frequently results in the loss of some of the metal dithizonate to the aqueous

wash solution. In some cases, part of the metal dithizonate may be converted to the enol form by the alkaline wash solution with resultant change in hue and intensity. If a photoelectric colorimeter is not available, the analyst will do well to investigate the titrimetric method.

## Limiting Conditions

No less than seventeen metals are known to form highly colored dithizonates, ranging in hue from violet through yellow and orange to red. This lack of specificity constitutes one of the most serious limitations of the reagent as an analytical tool. Actually, the prospect of using dithizone for the determination of a single metal is not nearly so hopeless as it might appear at first glance, since by the proper selection of conditions a remarkable selectivity may often be achieved. In the following representation of the equilibrium between dithizone and a reacting metal, where DzH represents dithizone, it is seen that a hydrogen ion is involved.

$$DzH + M^{+} \rightleftharpoons DzM + H^{+}$$

It may therefore be anticipated that the stability of a metal dithizonate, and therefore its extractability, is related to the pH of the solution. Kolthoff and Sandell (7) have shown experimentally that this is essentially true in the case of zinc and that the simple mass law applies to the extraction of this metal. Whether the extractability of other metals can similarly be related to the mass law has not been directly established. Empirically it has been demonstrated, however, that different pH limits exist for many of the metals outside of which they are not extracted. Thus, by simple adjustment of the pH, many analytical separations are possible. Wichman (8) has thoroughly summarized the possibilities.

Other expedients to improve selectivity are available. It has been established that the metal dithizonates are complexes of limited stability, and that masking agents may be chosen which form more stable complexes than dithizone with the various metals. In an alkaline solution of cyanide, for example, silver, mercury, cadmium, copper, nickel, zinc, and other metals are firmly complexed; in fact, only lead, thallium, tin, and bismuth are left extractable by dithizone. Similarly, only mercury, gold, and copper can be extracted from a weakly acid solution containing thiocyanate. Thus, by successive extractions from properly selected media, a high order of specificity may in many cases be achieved. Sandell (5) offers an excellent discussion of this.

## Effect of Impurities

The advent of dithizone, and, of course, of many other organic reagents of high sensitivity, has had a profound influence on the perspective of the analytical chemist. We now think of micrograms of a substance as an entirely adequate quantity for analysis. Whereas these high orders of sensitivity are often exceedingly useful, they do at the same time pose some serious practical problems. Most workers with dithizone soon come to the point of view that, "There is lead [for example] in everything." That this statement is literally true can now be convincingly demonstrated. In an analytical method where fractional micrograms are easily registered, it is axiomatic that blanks will be an important problem, and that unusual precautions must be taken to keep them proportionately low. In working with dithizone, there is a special blank problem beyond that usually encountered, arising from traces of metals present in the reagents. Small amounts of oxidizing agents readily convert dithizone to its related compound, diphenylthiocarbodiazone, which has an intense yellow color and is readily soluble in organic liquids. Its presence may readily be concealed by the metal dithizonate, but it contributes to the photometric reading none the less and in effect constitutes a blank. Liebhafsky and Winslow (9) offer the possibility that much of the "high blank" trouble

experienced by early workers may have been caused by the oxidation of dithizone rather than by casual contamination with metals.

### Elimination of Impurities

Much has been written concerning the purification of dithizone from its oxidation products (4), the removal of oxidants from chloroform and carbon tetrachloride (10) (11), and the removal of metals from reagents in general use. Bambach (12) discusses the purification of ammonium citrate, sodium sulfite, and potassium cyanide. Clifford and Wichman (4) discuss the purification of nitric acid, ammonium hydroxide, and distilled water.

Almost as troublesome as the persistent blank is the presence of traces of impurities in the reagents. A trace of sulfide, for example, may be exceedingly difficult to remove and leads to low results for many of the metals, because of the precipitation of the metal as sulfide.

Apparently, it was blank trouble which prompted Liebhafsky and Winslow (9) to state, "Our experience with dithizone as an analytical reagent indicates that satisfactory quantitative results on small samples can be obtained only through painstaking and somewhat tedious manipulation. For this reason it often will be advisable to use other methods of analysis where these will achieve the desired result." Doubtless there are many others sympathetic with this point of view. Certainly there are many analytical situations where the choice of the dithizone method, although possible, would not be advisable.

Despite the difficulties of the dithizone method, it is still apparent that in many cases where the highest order of sensitivity is required, dithizone remains the reagent *par excellence*. Those who have had the problem of determining lead or cadmium in foodstuffs, for example, require no persuasion.

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